(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification[7]: C08F 2/44, C08K 3/22

(21) International Application Number: PCT/AU03/00015

(22) International Filing Date: 8 January 2003 (08.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PR 9878   8 January 2002 (08.01.2002)   AU

(71) Applicants (for all designated States except US): COM-MONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, Australian Capital Territory 2612 (AU). ORICA AUSTRALIA PTY LTD [AU/AU]; 1 Nicholson Street, Melbourne, Victoria 3000 (AU).

(72) Inventors; and
(75) Inventors/Applicants (for US only): ELDRIDGE, Robert, James [AU/AU]; 20 Heath Street, Glen Waverley, Victoria 3150 (AU). NORRET, Marck [DK/DK]; Strandagervaenget 22, DK-7000 Fredericia (DK). DAHLKE, Thomas, W. [DE/DE]; Beroldingerweg 9, 79194 Gundelfingen (DE). BALLARD, Mathew, John [AU/AU]; 12 Stableford Avenue, Glen Waverley, Victoria

3150 (AU). ADAMS, Beryn, John [NZ/AU]; 6/28 Harold Street, Hawthorn East, Victoria 3123 (AU).

(74) Agents: ROBERTS, Mark, Kemball et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, Victoria 3000 (AU).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPLEXING RESINS AND METHOD FOR PREPARATION THEREOF

(57) Abstract: The invention provides a process for preparing polymeric beads of complexing resin incorporating magnetic particles, which process comprises: producing a dispersion having a continuous aqueous phase and a dispersed organic phase, said organic phase comprising one or more polymerisable monomers, magnetic particles and a dispersing agent for dispersing said magnetic particles in the organic phase; polymerising said one or more polymerisable monomers to form polymeric beads incorporating said magnetic particles, wherein said polymeric beads include amine groups capable of complexing a transition metal cation, or wherein said polymeric beads are reacted with one or more compounds to provide amine groups capable of complexing a transition metal cation, complexing resins prepared by this process, and polymeric beads of complexing resin comprising a polymer matrix having magnetic particles dispersed substantially uniformly therein, wherein the polymer matrix incorporates amine groups capable of complexing a transition metal cation.

- 1 -

COMPLEXING RESINS AND METHOD FOR PREPARATION THEREOF

The present invention relates to complexing resins and in particular, to polymeric beads of complexing resin incorporating magnetic particles and processes for their preparation. The

5   invention further relates to a method of separating transition metals from aqueous solutions using the complexing resin.

Ion exchange is widely used as a technique for removing both organic and inorganic species from water. Ion exchange techniques conventionally involve passing water

10   through a packed bed or column of ion exchange resin. Target species are removed by being adsorbed on to the ion exchange resin. Ion exchange resins are commonly used for removing contaminants from water.

Industrial wastewaters and mine drainage, etc, are often contaminated with dissolved

15   transition metal salts. Such metal contaminants must be removed before the water can be released to the environment because of the toxic effect most transition metals have on human beings and other living species. Increasingly, groundwater is becoming contaminated with transition metal compounds and requires similar treatment to comply with potable water guidelines. In such instances transition metal contaminants are

20   typically removed by precipitation with lime, caustic soda, sodium sulfide, or similar reagents. However, this process yields a voluminous sludge that must be dewatered and disposed of in a secure landfill.

Ion exchange would be preferable to precipitation because it could recover the transition

25   metal salts as an aqueous concentrate, which could potentially be recycled to a beneficial use. However, effective use of commercial ion exchange resins in such applications is currently not viable. In particular, most commercial resins are too slow to function effectively at short contact times. Treating substantial flows of water or liquid at adequate contact times requires very large columns and is therefore not economically feasible. Also,

30   commercial resins typically have a poor capacity utilisation due to their low selectivity for transition metals over ever-present innocuous background ions.

Ion exchange resins incorporating dispersed magnetic particles have been described as suitable for applications involving continuous high flows. In the absence of shear, attraction between the magnetic particles in the resin causes the resin beads to flocculate and settle rapidly, enabling such resins to be readily separated under demanding process

5   conditions. For such resins to operate effectively, the magnetic material should be incorporated in a manner that prevents its loss by erosion or dissolution during use. For this reason it is highly desirable that the magnetic material should be dispersed evenly throughout the polymeric bead. Improved mechanical strength is a further benefit of even particulate dispersion.

10

Processes for the manufacture of magnetic ion exchange resins have been described in some prior art patents. For example, United States Patent No. 2,642,514, discloses an ion exchange process using a mixed ion exchange resin. One of the ion exchange resins is a magnetic resin. The magnetic resin is produced by polymerising a reagent mix until a

15   viscous syrup is obtained. Magnetite is added to the viscous syrup and the mixture is agitated to mix in the magnetite. The mixture is cured to form a hard resin that is subsequently ground to form irregular particles of magnetic resin.

European Patent Application No. 0,522,856 also discloses the manufacture of magnetic ion

20   exchange resins by grinding or crushing a polymer having magnetite dispersed throughout the polymer matrix. The processes for producing magnetic ion exchange resins disclosed in U.S. 2,642,514 and EP 0,522,856 require a grinding step, which increases the cost and complexity of the process and increases losses due to the formation of polymer particles outside the desired particle size range during the grinding step. Further, the ground

25   particles are irregular in shape and easily abraded.

An alternative process for producing magnetic ion exchange resins is described in Australian Patent Application No. 60530/80. In this process, magnetic porous crosslinked copolymer particles are produced by a suspension polymerisation process. A mixture of

30   polymerisable vinyl compounds, magnetic powder, polymerisation initiator and dispersion stabiliser is dispersed in water and polymerised.

A similar process for producing magnetic ion exchange resins is described in Japanese Patent Application No. 62141071. In this process an electron donor substance such as polyvinyl pyridine-styrene copolymer, polyacrylamide-styrene copolymer or polyvinyl imidazole copolymer is preferably added to the mixture in order to stabilise the dispersion

5   of magnetic powder. According to the specification, the dispersion treatment is important for stabilising the dispersed state so that the rate of settling of the magnetic powder is reduced by breaking up magnetic particles which have clumped together in secondary or larger particles into primary particles. Furthermore, it is necessary to use dispersion equipment which differs from normal mixing equipment, with special mixers being

10   required.

Many of the aforementioned difficulties associated with producing magnetic ion exchange resins can be overcome by using the process disclosed in Australian patent No.704376. This patent describes an aqueous suspension polymerisation process which involves

15   polymerising a dispersed organic phase comprising monomer, magnetic powder and a dispersing agent. During polymerisation the dispersing agent reacts with monomer to become covalently bound within the resin. By this process, spherical polymeric beads having an even distribution of magnetic powder throughout can be produced. The patent indicates that resins suitable for separating transition metals can be prepared by hydrolysis

20   of poly(ethyl acrylate) beads, thereby providing a weak acid cation exchange resin.

While providing an effective process to prepare magnetic ion exchange resins, the resins contemplated in Australian patent No.704376 are not particularly suitable for use in separating transition metals from aqueous solutions as they would have poor capacity

25   utilisation due to their low selectivity for transition metals over innocuous background ions.

Commercial weak base resins, usually used as anion exchangers, provide means for the selective adsorption of transition metal salts over innocuous background ions, for example

30   alkali and alkaline earth metals such as Na^+, Ca^{2+} or Mg^{2+}, when used as complexing resins, in their free base form. However, such resins are not suited to continuous high

flows. In particular, the resins would be difficult to recover from the treated water and their large size, typically 0.5-1.2mm, provides a relatively slow adsorption rate, especially at low ion concentrations.

5   Accordingly, there is a need to develop complexing resins that are particularly suited to selectively removing transition metals from continuous high flows.

According to a first aspect the present invention provides a process for preparing polymeric beads of complexing resin incorporating magnetic particles, which process

10   comprises: producing a dispersion having a continuous aqueous phase and a dispersed organic phase, said organic phase comprising one or more polymerisable monomers, magnetic particles and a dispersing agent for dispersing said magnetic particles in the organic phase; polymerising said one or more polymerisable monomers to form polymeric beads incorporating said magnetic particles, wherein said polymeric beads include amine

15   groups capable of complexing a transition metal cation, or wherein said polymeric beads are reacted with at least one or more compounds to provide amine groups capable of complexing a transition metal cation.

In a second aspect the present invention provides polymeric beads of complexing resin

20   comprising a polymer matrix having magnetic particles dispersed substantially uniformly therein, wherein the polymer matrix incorporates amine groups capable of complexing a transition metal cation.

The process of the present invention advantageously provides the ability to form spherical

25   polymeric beads of complexing resin that have magnetic particles which are substantially evenly distributed throughout the polymeric beads. In addition, the present invention provides for the preparation of polymeric beads comprising complexing amine groups which are suitable as complexing resins and demonstrate an ability to selectively remove transition metals from aqueous solutions in the presence of innocuous background ions

30   under continuous high flow conditions.

- 5 -

In accordance with the process of the present invention the organic phase is the dispersed phase. The organic phase includes one or more polymerisable monomers that polymerise to form the polymer matrix of the polymeric beads. It is preferred that the polymer matrix is a copolymer based on two (or more) monomers. Generally the polymeric beads will be prepared from two types of polymerisable monomers:

      (a)   crosslinking monomers which are able to provide crosslink points; and

      (b)   functional monomers which are able to provide functional groups.

By the process of the invention, the organic phase preferably includes crosslinking monomers and functional monomers. Some monomers, such as bis(diallylamino)alkanes or bis(acrylamidoethyl)amine can function as both crosslinking monomers and functional monomers. The functional monomers may be amine functionalised polymerisable monomers that provide the necessary amine groups to enable the polymeric beads to act as a complexing resin. The functional monomers may provide polymeric beads with sites that can be later reacted with one or more compounds to provide the necessary amine groups that will enable the polymeric beads to act as a complexing resin. The polymer matrix of the beads may be a copolymer matrix. Accordingly, other monomers may be included in the organic phase to copolymerise with the crosslinking monomers and the functional monomers, for example backbone monomers may be included.

The cross-linking monomers may be selected from a wide range of monomers, including divinyl monomers such as divinyl benzene, ethyleneglycol dimethacrylate or poly(ethyleneglycol) dimethacrylate or methylene bisacrylamide, ethyleneglycol divinylether and polyvinyl ester compounds having two or more double bonds, such as trimethylolpropane triacrylate or trimethacrylate. This list is not exhaustive.

A wide range of functional monomers may also be used in the process of the present invention. Suitable monomers include glycidyl methacrylate, vinyl benzyl chloride, methyl acrylate, N-vinyl formamide, dimethylaminoethyl methacrylate, aminopropyl acrylamide and methacrylamide, N,N-dimethylaminopropyl acrylamide and

- 6 -

methacrylamide, vinyl pyridine and organic-soluble diallylamine or vinylimidazole salts. This list is not exhaustive.

The backbone monomers include any monomer polymerisable by free radicals such as
5   styrene, vinyl toluene, methyl methacrylate and other acrylates and methacrylates. This list is not exhaustive.

In order to increase the efficiency of removal of transition metals from water being treated by the complexing resin, it is preferred that the polymeric beads are macroporous. This
10   increases the total surface area of each bead available for contact.   To produce macroporous polymeric beads according to the present invention, the dispersed phase should include one or more porogens. The porogen becomes dispersed throughout the droplets that form the dispersed phase, but the porogen does not take part in the polymerisation reaction. Accordingly, after the polymerisation reaction is completed, the
15   porogen can be removed from the polymeric beads, for example by washing or steam stripping, to produce macroporosity in the polymeric beads.

Suitable porogens for use in the process of the present invention include aromatic compounds such as toluene and benzene, alcohols such as butanol, iso-octanol,
20   cyclohexanol, dodecanol, isoamyl alcohol, tert-amyl alcohol and methyl iso-butyl carbinol, esters such as ethyl acetate and butyl acetate, saturated hydrocarbons such as n-heptane, iso-octane, halogenated solvents such as dichloroethane and trichloroethylene, plasticisers such as dioctylphthalate and dibutyl adipate, polymers such as polystyrene and polyvinyl acetate; and mixtures thereof. Mixtures of cyclohexanol with other porogens such as
25   dodecanol or toluene have been found to be especially suitable for use as a porogen in the process of the present invention. It will be appreciated that the above list of porogens is not exhaustive and that the invention encompasses the use of other porogens and other combinations of porogens.

30   Incorporation of magnetic particles into the polymeric beads results in the beads becoming magnetic. Magnetic separation techniques may be used to conveniently separate the beads

from a solution or liquid being treated. The magnetic particles used in this embodiment of the present invention may be any solid material that is magnetic. Examples include γ-iron oxide (γ-Fe$_2$O$_3$, also known as maghemite), magnetite (Fe$_3$O$_4$), chromium dioxide, other metal oxides and more exotic magnetic materials, such as those based on neodymium or samarium and other rare earth materials, for example samarium-cobalt or neodymium iron boride. Maghemite is especially preferred because it is inexpensive.

The magnetic material is added during the process in the form of particles and it may or may not be magnetised upon addition. The particle size of the particles may range up to a size that is up to one-tenth of the particle size of the polymeric beads formed in the process of the present invention. Particles that are larger than that may be difficult to evenly disperse into the polymeric beads. More preferably, the particles of magnetic material range in size from sub-micron (e.g.0.1μm) to 500μm, most preferably from 0.1μm to 10μm.

The process of the present invention includes a dispersing agent for dispersing the magnetic particles in the dispersed phase. The dispersing agent acts to disperse the magnetic particles in the droplets of the dispersed phase to thereby form a stable dispersion (or suspension) of the magnetic particles in the dispersed phase. The dispersing agent also acts to promote a substantially even distribution of magnetic particles throughout the resultant polymeric beads. In this regard, the problem of erosion of the magnetic particles from the polymeric beads in service, as may happen if the magnetic particles were located only on the outer surface of the beads is avoided, or at least alleviated. Suitable dispersing agents will generally have a good binding affinity toward the surface of the magnetic particles and preferably should be able to chemically bond to the surface of the particles. The dispersing agent will also generally be soluble in the one or more polymerisable monomers. Preferably, the dispersing agent reacts with one or more of the monomers to become covalently bound within the polymer matrix. Use of a dispersing agent of this type not only results in a substantially even distribution of magnetic particles throughout the polymeric bead, but the particles also advantageously become more effectively bound within the bead through the dispersing agent being covalently bound to the polymer

- 8 -

matrix. In this case, the problem of leaching of the magnetic particles from the polymeric beads can be avoided, or at least alleviated. Selection of the dispersing agent will typically depend upon the particular magnetic material and monomers being used. Persons skilled in the art should be able to readily select a suitable dispersing agent having regard to the specific reaction system employed.

The polymerisation reaction that takes place in the process of the present invention is a suspension polymerisation reaction and techniques known to those skilled in the art to control and monitor such suspension polymerisation reactions apply to the present invention. In order to maintain the dispersed phase in the form of a suspension of droplets in the continuous phase whilst avoiding aggregation of the droplets, a stabilising agent is preferably used. Suitable stabilising agents may include polyvinyl alcohol, polyvinyl pyrrolidone, gelatine, methyl cellulose or sodium polyacrylate. It is to be understood that the invention extends to cover any stabilising agent that may be suitable for use. The stabilising agent is typically present in an amount of 0.01 to 5% by weight, and preferably 0.05 to 2% by weight, based on the weight of the whole mixture.

It will also be generally necessary to use an initiator to initiate the polymerisation reaction. The initiator to be used depends upon the monomers present in the reaction mixture and the choice of initiator and the amount required will be readily apparent to the skilled addressee. By way of example only, suitable initiators include azoisobutyronitrile, benzoyl peroxide, lauroyl peroxide and t-butyl hydroperoxide. The amount of initiator used is generally in the range of 0.01 to 5 wt %, more preferably 0.10 to 1%, calculated on the total weight of monomer(s).

In a preferred embodiment of the present invention, the monomer mixture may include a functional monomer present in an amount of from 10 to 99% by weight, based upon the weight of total monomers, more preferably 50 to 90% by weight (same basis). The crosslinking monomers may be present in an amount of from 1 to 90% by weight, based on the weight of total monomers, more preferably 10 to 50% by weight (same basis). Additional monomers may be present in an amount of 0 to 60% by weight, more

preferably 0 to 30% by weight, based on the weight of total monomers. The total monomers may constitute from 1 to 50%, more preferably 5 to 30% by weight of the whole suspension polymerisation mixture.

5   The magnetic particles are preferably added in an amount of from 10 to 300 wt%, based on the weight of total monomers, more preferably 20 to 100% by weight (same basis). The dispersing agent is preferably added in an amount of 0.10 to 30% by weight, more preferably 1 to 10% by weight, based on the weight of magnetic particles.

10   The dispersion of the dispersed phase (which includes the monomer(s)) in the continuous phase is usually achieved by mixing the organic and aqueous phases and shearing the resulting mixture. The shear applied to the dispersion can be adjusted to control the size of the droplets of the dispersed phase. As the droplets of dispersed phase are polymerised to produce the polymeric beads, the shear applied to the dispersion largely controls the

15   particle size of the polymeric beads. Generally, the polymeric beads are controlled to have a particle size in the range of 10-5000μm.

Once a stable dispersion of dispersed phase in continuous phase is established, the polymerisation reaction is started by heating the dispersion to the desired reaction

20   temperature. The dispersion may be held at the desired reaction temperature until the polymerisation reaction is substantially complete.

Depending upon the monomers used, once the polymerisation is complete, the resulting polymeric beads may include amine groups that will enable the polymeric beads to act as a

25   complexing resin, the amine groups being provided by the polymerised residues of one or more of the functional monomers. Functional monomers capable of introducing amine functionality to the beads include, but are not limited to, dimethylaminoethyl methacrylate, aminopropyl acrylamide and methacrylamide, N,N-dimethylaminopropyl acrylamide and methacrylamide, vinyl pyridine, organic-soluble diallylamine or vinylimidazole salts.

30

- 10 -

Alternatively, once the polymerisation is complete, the resulting polymeric beads may require subsequent treatment to provide the amine groups that will enable the polymeric beads to act as a complexing resin. The particular treatment process used will be dependent on the composition of the polymeric beads to be treated. Generally, the treatment process will involve reacting the polymeric beads with one or more compounds that convert functional groups present on the beads to amine groups or reacting functional groups on the beads with one or more compounds that introduce amine groups to the beads.

In the treatment process where functional groups on the beads are converted to amine groups, various combinations of suitable functional groups and reactants may be employed, the nature of which would be known to those skilled in the art. It is preferable that the functional groups on the beads are amide groups and more preferable that the amide groups are introduced to the polymeric beads by way of an amide functional monomer. Exemplary amide functional monomers include, but are not limited to, N-vinyl formamide or N-methyl-N-vinyl acetamide. Amide groups can be readily converted to amine groups by hydrolysis, Hofmann degradation or borohydride reduction, hydrolysis is a preferred technique. For example, amide groups in N-vinylformamide or N-methyl-N-vinylacetamide monomer units can be converted to amine groups by hydrolysis.

In the treatment process where functional groups on the beads are reacted to introduce amine groups, various combinations of suitable functional groups and reacting compounds may be employed, the nature of which would be known to those skilled in the art. Preferred functional groups on the beads include, but are not limited to, halogens, epoxides, esters and amides. It is preferable that such functional groups are introduced to the polymeric beads by way of appropriate functional monomers. Exemplary functional monomers in this regard include, but are not limited to, vinyl benzyl chloride, glycidyl methacrylate, acrylate or methacrylate esters or amides. Such functional groups can be reacted with compounds that introduce amine groups. Suitable compounds include, but are not limited to, amines, diamines, and polyamine compounds and their respective salts. Preferred compounds for introducing amine groups include, but are not limited to,

- 11 -

piperidine,   N,   N-diethylethylene   diamine,   dimethylamine,   diethylamine, dimethylaminopropylamine, ethylenediamine, diethylenetriamine, polyethyleneimine and their respective salts.

5   The complexing properties of the polymeric beads will be primarily dictated by the nature of the amine groups present therein.   Such amine groups should be readily accessible to undergo complexation with transition metal cations.   It will be appreciated by those skilled in the art that amine groups to be included in the polymeric beads, either by direct polymerisation or by subsequent treatment, have little or no affinity to complex with alkali

10   and alkaline earth metal cations, but can readily complex with transition metal cations. Those skilled in the art will also appreciate that the selection of amine groups to be included in the polymeric beads will be dependent on both the nature of the species to be separated and the nature of background ions present in the solution.   For example, selectivity may be affected by factors such as steric crowding of the nitrogen atoms,

15   electron density on the nitrogen atoms and the availability of multiple nitrogen atoms to form chelate complexes.

The beads may require cleaning prior to a subsequent treatment or prior to being used. This may be achieved by a sequence washing steps or by steam stripping the beads.

20
One method for cleaning the polymeric beads includes the following steps:

   (a)   add reaction product to a large excess of water, stir and allow to settle;

   (b)   separate beads from the supernatant;

   (c)   add separated beads to a large excess of water, stir and allow to settle before

25   separating beads from the supernatant;

   (d)   repeat step (c) several times;

   (e)   disperse water washed beads in alcohol (ethanol);

   (f)   separate beads from alcohol and dry.

30   An alternative clean-up procedure is to steam strip the porogens and then wash the polymeric beads to remove any free solid particulate material.

- 12 -

In an especially preferred embodiment of the invention the polymeric beads are formed as a copolymer of glycidyl methacrylate and divinyl benzene. The monomers reside in the organic phase, which also includes a mixture of cyclohexanol with toluene or dodecanol as porogens. Polyvinyl alcohol is used as a stabilising agent. A free radical initiator such as

5   "VAZO" 67 or Azoisobutyronitrile (AIBN) is added to the organic phase as a polymerisation initiator and γ-iron oxide is the magnetic material. The solid phase dispersing agent preferred for use in this system is a block copolymer of poly(hydroxystearic acid) and poly(ethyleneimine) and sold under the trade name SOLSPERSE 24000. This solid phase dispersing agent has a high binding affinity for the

10   surface of the γ-iron oxide. It is believed that primary and secondary amino groups present in the dispersing agent provide this high binding affinity. Residual primary and secondary amino groups present in the dispersing agent are also believed to react with the epoxy group of the glycidyl methacrylate, while the vinyl groups from the methacrylate react with polymerising radicals to become covalently bound to the polymer matrix. All of the

15   components of the organic phase are preferably pre-mixed in a separate tank and dispersed in water in the reaction tank. Once the polymerisation reaction is substantially complete, the resultant polymeric beads are subsequently reacted with an amine compound such as piperidine or N,N-diethylethylenediamine or their respective salts to produce a complexing resin. Reaction with the amine compound may be promoted or accelerated by heating.

20

In another aspect, the present invention provides a process which produces polymeric beads of complexing resin incorporating magnetic particles which further incorporate a toughening agent. The toughening agents are selected to increase the impact resistance of the resin. General techniques for increasing toughness of polymer materials may be

25   readily employed in the process of the present invention to afford polymeric beads with increased durability. For example, rubber toughening agents may be used to improve the strength and durability of glycidyl methacrylate-based polymeric beads. The use of these rubber toughening agents is believed to result in improved durability and an increased service life of the polymeric beads. The rubber toughening agents include low molecular

30   weight rubbers which may be incorporated into the dispersed phase. A particularly

- 13 -

preferred rubber toughening agent is sold under the trade designation Kraton D1102 although other commercially available rubber toughening agents can be used.

In another aspect, the present invention provides a method of separating transition metal ions from an aqueous solution comprising contacting said solution with polymeric beads of complexing resin according to the present invention. The metal-loaded beads may then be magnetised, causing them to aggregate and settle out of the treated solution. Alternatively, they can be separated on a wet high intensity magnetic separator or magnetic drum separator or similar device.

As mentioned above the polymeric beads of complexing resin of the present invention are preferably macroporous. The particle size of the polymeric beads is preferably within the range of 30μm to 1000μm. The particles of solid material may have a particle size in the range of sub-micron (e.g. 0.1μm) to 500μm and more preferably from 0.1μm to 10μm.

The dispersing agent is a chemical compound or species that can react with at least one of the monomers used to produce the polymer matrix such that the dispersing agent is covalently bound within the polymer matrix. Further, the dispersing agent should have a good affinity for the surface of the magnetic particles and preferably should be able to chemically bond to the surface of the magnetic particles. The use of such an agent allows the magnetic particles to be dispersed throughout the polymer matrix.

As the magnetic particles are dispersed throughout the polymeric beads of the present invention, the magnetic particles are not easily removed from the beads and this allows the beads to be subjected to a number of handling operations, such as conveying, pumping and mixing, without substantial erosion of solid particles therefrom.

The invention will be further described with reference to the following non-limiting Examples.

- 14 -

Example 1: Preparation of piperidine functionalised magnetic macroporous complexing resin.

Magnetic macroporous complexing resins were prepared in accordance with the process of the present invention using the following raw materials:

5   1.   **Water**: this is the continuous medium in which the organic phase is dispersed and then reacted.

2.   **Gohsenol ® GH 20** (available from Nippon Gohsei) this is a high molecular weight polymeric surfactant, a polyvinyl alcohol, that disperses the organic phase in the water as droplets.

10   3.   **Kraton D1102** (available from Shell Chemical Company): this acts to improve the strength and durability of the resin.

4.   **Cyclohexanol**: this is the major porogen: it is a solvent for the monomers, but a non-solvent for the polymer, and it promotes the formation of voids and internal porosity in the resin beads.

15   5.   **Toluene**: this is the minor porogen.

6.   **Solsperse ® 24000** (available from Avecia Pigments & Additives): it is a solid phase dispersing agent and is a block copolymer of poly(hydroxystearic acid) and poly(ethyleneimine).

7.   **Pferrox ® 2228HC γ-Fe$_2$O$_3$** (available from Pfizer): gamma-iron oxide
20   (maghemite). This is the magnetic oxide that makes the resin beads magnetic.

8.   **DVB-50 (divinyl benzene)**: this is the monomer that crosslinks the beads.

9.   **GMA (glycidyl methacrylate)**: this monomer is polymerised to form part of the polymer matrix. The polymerised residue of the monomer provides epoxy groups within the matrix that can be subsequently reacted to produce a complexing resin as
25   follows:

polymerisation

AIBN, heat

amination
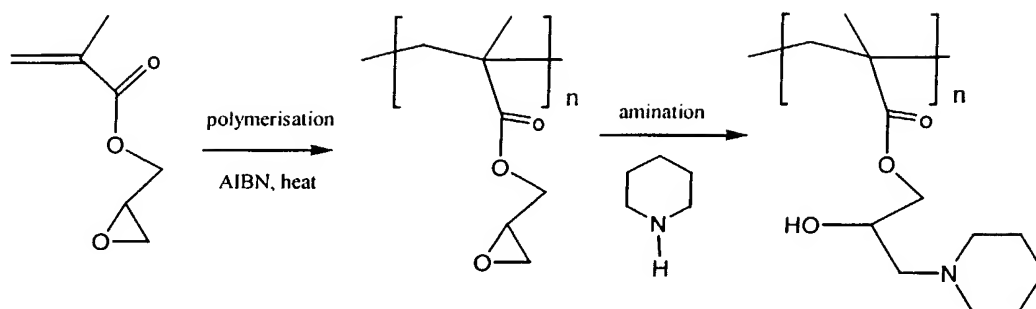
10.   **VAZO ® 67** (available from Dupont): this is the polymerisation initiator, which activates when the mixture is heated above 75°C.

5   11.   **Piperidine**: this is the amine that reacts with the epoxy group provided by the polymerised residue of glycidyl methacrylate to form complexing groups.

12.   **Ethanol**: this is used as a rinse and as a wetting agent.

10   Method

Toluene (1.4kg), cyclohexanol (5.5kg) and Solsperse 24000 (2.5kg) were charged to a mix tank. The solution was then stirred slowly with a Cowles-type dispersing blade while Pferrox 2228 HC γ-Fe$_2$O$_3$ (13kg) was added. The speed was increased and held for a time sufficient to break up the large aggregates. This mix was then passed through a closed-

15   head bead mill with sufficient residence time to ensure that the majority of the particles were smaller than 5 μm in size. In a separate mix tank, toluene (2.6kg), cyclohexanol (1.6kg) and Kraton D1102 (1kg) were added and stirred until the rubber had dissolved. The solution of rubber was then added to the pigment dispersion and mixed until it was homogeneous.

20

Water (110L) was charged to a 250L reactor and the stirrer and nitrogen purge started. Next Gohsenol ® GH-20 (400g) was added, and the water phase heated to 80°C to dissolve the surfactant. While the water was heating the prepared pigment and rubber solution was charged to a separate stirred mix tank and the stirrer turned on. Glycidyl methacrylate

25   (21kg), divinylbenzene (5.2kg) and cyclohexanol (14kg) were added in turn. A solution of Vazo 67(100g) in toluene (100g) was then added, and the mixture was stirred for a further

five minutes before adding it to the heated water phase. The resulting dispersion was held at 80°C (±5°C) for two hours, during which time polymerisation occurred and solid resin beads (44kg) were formed.

5   The resultant beads contained 25% by weight of γ-Fe_2O_3 and had a mean particle diameter of 225 μm, with a standard deviation of 100 μm. A portion of this resin was cleaned of the excess γ-Fe_2O_3 and organic solvent by repeated cycles of washing, settling and decanting. 50 mL (16g) of this resin was then slurried in 100 mL of water and heated to 85 °C. Piperidine (6.8 g, 80 mmol) was added and the mixture heated at 85 °C under nitrogen for

10   four hours. The beads were then washed and a sample dried under vacuum at 60 °C and weighed. Wet resin was treated successively with 1 M sodium chloride solution acidified to pH 1; water; 0.2 M potassium nitrate solution; water; 0.1 M sodium hydroxide solution; water; neutral 1 M sodium chloride solution; water; 0.2 M potassium nitrate solution. The chloride ions displaced by potassium nitrate were titrated with silver nitrate, yielding a

15   total capacity of 2.11 meq/g and a strong base capacity of 0.10 meq/g. The weak base capacity is therefore 2.01 meq/g.

The maghemite was well dispersed throughout the resin beads produced in this Example.

20   Example 2:   Preparation of N,N-diethylethylene diamine functionalised magnetic macroporous complexing resin.

Magnetic macroporous complexing resins were prepared in a similar fashion to Example 1, except the solid resin beads (16g) were aminated with N, N-diethylethylene diamine

25   (DEDA, 9.3g, and 80 mmol) instead of piperidine.

Example 3: Evaluation of copper uptake as a function of pH by complexing resin prepared in Example 1

30   The complexing performance of resin prepared in Example 1 was assessed by measuring copper uptake as a function of pH. The resin sample was treated with 1 M sodium

hydroxide solution to ensure that weak base groups were in the free base form, then rinsed with water. Samples were equilibrated with copper (II) sulfate solutions initially containing 0.5 mmol Cu(II) per meq of weak base capacity and ranging in pH from 2 to 5. The uptake of copper varied from 0.17 mmol per gram of resin at pH 2 to 0.43 mmol/g at

5   pH5 as shown in Table 1. (At higher pH copper hydroxide precipitated).

Table 1

pH	Copper Uptake (mmol/g)
2	0.17
3	0.18
4	0.34
5	0.43

10   Example 4:   Evaluation of copper uptake by complexing resin prepared in Example 2 in the presence or absence of $MgSO_4$

The complexing performance and chelate selectivity of the resin prepared in Example 2 was assessed by measuring copper uptake as a function of copper concentration, in

15   solutions with and without magnesium sulfate. The resin was treated with 1 M NaOH and rinsed. Samples were then equilibrated at pH with $CuSO_4$ having initial concentrations ranging from 1 to 40 mM. The experiment was repeated with a second series of $CuSO_4$ solutions, which also contained magnesium sulfate at a concentration of 27 mM. The uptakes of copper in the two experiments were very similar, reaching approximately 0.22

20   mmol/g at equilibrium $CuSO_4$ concentrations above 13 mM (Table 2). More than 90% of the adsorbed copper was desorbed in about 15 bed volumes of 0.1 M hydrochloric acid. The required volume of acid decreases with increasing acid concentration, with slight losses of iron oxide from the beads at high concentration.

25

- 18 -

Table 2

Copper Concentration (mmol/L)	Copper Uptake no MgSO$_4$ (mmol/g)	Copper Uptake with MgSO$_4$ (mmol/g)
0.01	-	0.03
0.06	0.08	-
0.07	-	0.11
0.12	0.05	-
0.18	-	0.08
0.20	-	0.135
0.31	0.125	-
2.74	0.195	-
3.42	-	0.19
11.0	0.23	-
13.4	-	0.225
28.6	0.26	-

Example 5:   Evaluation of zinc and cadmium uptake by complexing resins prepared in Examples 1 and 2

5

The uptake of zinc and cadmium by resins prepared in Examples 1 and 2 were evaluated. The resins from Examples 1 and 2, after treatment with 1 M NaOH solution, were equilibrated with zinc sulfate and cadmium sulfate solutions having initial concentrations ranging from 1 to 40 mM. At pH 6 and equilibrium ZnSO$_4$ concentrations about 6 mM the piperidine resin adsorbed 0.22 and the DEDA resin 0.3 mmol Zn/g. Maximum cadmium uptakes were 0.29 and 0.35 mmol/g. Both resins were more than 90% regenerated with 12-18 bed volumes of 0.1 M HCl.

10

15

Example 6: Comparison of the uptake rate of complexing resins prepared in Examples 1 and 2 with a commercial complexing resin

The uptake rates of resins prepared in Examples 1 and 2 were evaluated and compared with values obtained using a commercial polyamine complexing resin (Fuji PEI-CS-07). Resins from Example 1 and 2 (40 mL), after treatment with 1 M NaOH solution, were suspended in 50mL of water with continuous stirring and $CuSO_4$ or $CdSO_4$ (0.5 mol per mol of weak base group) added. The disappearance of metal ions was monitored as a function of time. For comparison the copper uptake experiments were repeated with the commercial polyamine resin Fuji PEI-CS-07. The piperidine-functionalised resin removed 50% of the added copper in 30 seconds at pH 5 and essentially all of it in less than 50 minutes (Table 3). Uptake of cadmium at pH 6 reached 50% in about 15 seconds and 95% after about 45 minutes (Table 4). Uptake of copper on the DEDA-functionalised resin at pH 5.4 reached 50% in less than 30 seconds and essentially 100% in less than an hour (Table 5). In contrast, the commercial resin adsorbed only 35% of the copper in one hour and had not reached equilibrium after 72 hours (Table 6).

Table 3

Time (min)	Fraction of Copper Remaining ($[Cu]/[Cu]_0$)
0	1
1	0.212
5	0.176
10	0.061
15	0.049
30	0.017
45	0.00

20

Table 4

Time (min)	Fraction of Cadmium Remaining ($[Cd]/[Cd]_0$)
0	1
5	0.101
10	0.088
30	0.060
45	0.055
60	0.041

Table 5

Time (min)	Fraction of Copper Remaining ($[Cu]/[Cu]_0$)
0	1
1	0.19
5	0.10
10	0.077
15	0.039
30	0.019
45	0.015
60	0.007
120	0.010
300	0.007
430	0.002

5

10

Table 6

Time (min)	Fraction of Copper Remaining ($[Cu]/[Cu]_0$)
0	1
5	0.92
10	0.82
15	0.87
30	0.74
45	0.68
60	0.64
120	0.56
210	0.53
1200	0.59

It will be appreciated that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention encompasses all such variations and modifications that fall within the spirit and scope.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

- 22 -

THE CLAIMS:

1.   A process for preparing polymeric beads of complexing resin incorporating magnetic particles, which process comprises: producing a dispersion having a continuous aqueous phase and a dispersed organic phase, said organic phase comprising one or more polymerisable monomers, magnetic particles and a dispersing agent for dispersing said magnetic particles in the organic phase; polymerising said one or more polymerisable monomers to form polymeric beads incorporating said magnetic particles, wherein said polymeric beads include amine groups capable of complexing a transition metal cation, or wherein said polymeric beads are reacted with one or more compounds to provide amine groups capable of complexing a transition metal cation.

2.   The process according to claim 1 wherein the organic phase comprises two or more monomers.

3.   The process according to any one of claims 1 to 2 wherein said one or more polymerisable monomers are selected from:

        (a)   crosslinking monomers which are able to provide crosslink points; and
        (b)   functional monomers which are able to provide functional groups.

4.   The process according to claim 3 wherein said functional monomer provides amine groups capable of complexing a transition metal cation.

5.   The process according to claim 4 wherein said functional monomer provides amine groups selected from dimethylaminoethyl methacrylate, aminopropyl acrylamide and methacrylamide, N,N-dimethylaminopropyl acrylamide and methacrylamide, vinyl pyridine, organic-soluble diallylamine or vinylimidazole salts.

6.   The process according to claim 3 wherein said functional monomer includes a functional group capable of reaction with one or more compounds to provide said amine

- 23 -

groups capable of complexing a transition metal cation.

7.   The process according to claim 6 wherein said functional monomer capable of providing amine groups includes an amide group.

8.   The process according to claim 7 wherein said functional monomer including an amide group is selected from N-vinyl formamide and N-methyl-N-vinyl acetamide.

9.   The process according to claim 6 wherein said functional monomer capable of providing amine groups includes an epoxy group.

10.   The processing according to claim 9 wherein said functional monomer including an epoxy group is glycidyl methacrylate.

11.   The process according to claim 6 wherein said functional monomer capable of providing amine groups is a vinyl ester.

12.   The process according to claim 11 wherein said vinyl ester is selected from acrylate or methacrylate esters.

13.   The processing according to claim 12 wherein the acrylate ester is methyl acrylate.

14.   The process according to any one of claims 1 to 13 wherein said one or more polymerisable monomers further includes one or more back bone monomers.

15.   The process according to any one of claims 1 to 14 wherein said dispersed organic phase further comprises a porogen.

16.   The process of any one of claims 1 to 15 wherein the magnetic particles are selected from γ-iron oxide, magnetite and chromium dioxide.

- 24 -

17.   The process according to any one of claims 1 to 16 wherein the dispersion is stabilised using a stabilising agent.

18.   The process according to any one of claims 1 to 17 wherein the dispersing agent
5   reacts with at least one monomer to become covalently bound within the polymeric beads.

19.   Polymeric beads of complexing resin comprising a polymer matrix having magnetic particles dispersed substantially uniformly therein, wherein the polymer matrix incorporates amine groups capable of complexing a transition metal cation.

10

20.   The polymeric beads of claim 19, wherein the polymeric matrix incorporates a dispersing agent covalently bound within the polymeric matrix.

21.   A complexing resin prepared by the process of any one of claims 1 to 18.

15

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]:   C08F 2/44;   C08K 3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT and   JAPIO
IPC as above AND Keywords:- magnetic, amine, particle, bead plus like terms.

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	AU 200181904 A (BAYER AKTIENGESELLSCHAFT) 21 January 2002 Examples 1 and 2	19, 20
X	US 4269760 A (Wakimoto et al.) 26 May 1981 Examples 10, 24	1-6, 9-15, 17-21
X	US 4123396 A (Rembaum et al.) 31 October 1978 Column 2 lines 50-51; Example 1	19, 20

☒	Further documents are listed in the continuation of Box C	☒	See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 10 February 2003	Date of mailing of the international search report **1 3 FEB 2003**
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **N.L. KING** Telephone No : (02) 6283 2150

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 522 856 A (BRADTEC LIMITED) 13 January 1993 Entire document	1-21
A	US 5900146 A (Ballard et al.) 4 May 1999 Entire document	1-21
A	US 4447475 A (Lubbock et al.) 8 May 1984 Entire document	1-21
A	US 2642514 A (Herkenhoff) 16 June 1953 Entire document	1-21
A	Patent Abstracts of Japan, JP 6-102709 A (MITA IND CO LTD) 15 April 1994 Abstract	1-21

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
AU	200181904	WO	200204555	DE	10033583		
US	4269760	CA	1124916	DE	2927249	FR	2430427
		GB	2029425	JP	55080404		
EP	522856	CA	2073568	CZ	9202169	GB	9115018
		HK	1005435	SK	2169/92	US	5397476
US	4123396	US	4197220				
US	5900146	WO	9607675	AU	34656/95	BR	9509161
		EP	779899	NO	971072	NZ	292471
		CN	1159198				
US	4447475	WO	8002687	AU	534337	GB	2061293
		EP	29443				

END OF ANNEX